

Binary Adsorption of Reactive Red 120 and Yellow 81 on *Spirogyra majuscula*

Abuzer Çelekli^{*1}, Mehmet Yavuzatmaca², Hüseyin Bozkurt³

^{*1}Department of Biology, Faculty of Art and Science, University of Gaziantep, 27310 Gaziantep, Turkey

²Department of Biology, Faculty of Art and Science, University of Abant İzzet Baysal, 14280 Bolu, Turkey

³Department of Food Engineering, Faculty of Engineering, University of Gaziantep, 27310 Gaziantep, Turkey

^{*1}celekli.a@gmail.com; ²y.zilan@hotmail.com; ³hbozkurt@gantep.edu.tr

Abstract- Binary adsorption of Reactive Red (RR) 120 and Reactive Yellow (RY) 81 on *Spirogyra majuscula* was performed as function of initial dye concentration, pH regimes, and contact time. Characterization of this alga was confirmed by FTIR spectrum. Increasing initial dye concentrations caused to increase ($p < 0.01$) in dye uptakes. Pseudo second-order kinetic model was well to describe the adsorption behavior of reactive dyes. Freundlich and Redlich-Peterson models were more suitable for the adsorption of RR 120, while for the adsorption of RY 81, Langmuir was more appropriate model. Therefore, it could be concluded that the adsorption of RR 120 could be accomplished due to heterogeneous adsorption phenomenon, whereas the adsorption of RY 81 was due to a homogeneous adsorption with monolayer surface coverage. Despite adsorption of these dyes in binary system, this alga could be used as an adsorbent for textiles wastewater treatment without adding extra cost.

Keywords- Adsorption; Reactive Red 120; Reactive Yellow 81; *Spirogyra majuscula*

Abbreviations

a_{R-P}	Redlich-Peterson isotherm constant ($L \text{ mg}^{-1}$) ^{β}
b	Langmuir constant ($L \text{ mg}^{-1}$)
β	exponent in Redlich-Peterson isotherm
C_{eq}	equilibrium dye concentration in solution (mg L^{-1})
C_o	initial dye concentration (mg L^{-1})
k_1	pseudo first-order rate constant ($L \text{ min}^{-1}$)
k_2	pseudo second-order rate constant ($g \text{ mg}^{-1} \text{ min}^{-1}$)
K_F	Freundlich adsorption capacity [$(\text{mg/g})(\text{mg L}^{-1})^{-\frac{1}{n}}$]
K_{R-P}	Redlich-Peterson isotherm constant ($L \text{ mg}^{-1}$)
n	Freundlich adsorption intensity
q_{eq}	amount of adsorbed dye per unit weight of biomass at equilibrium (mg/g)
q_{exp}	experimental amount of adsorbed dye at equilibrium (mg g^{-1})
q_{cal}	calculated amount of adsorbed dye for kinetics models (mg g^{-1})
q_o	maximum adsorption dye capacity form Langmuir model (mg g^{-1})
q_t	amount of dye per unit of biomass at time t (mg g^{-1})
RR	reactive red
RY	reactive yellow
R^2	correlation coefficient
R_L	a dimensionless constant for the Langmuir model
t	time (h)
p	significance level obtained from ANOVA

χ^2 chi-square test statistic

I. INTRODUCTION

Various industries such as plastic, food, cosmetic, carpet, paper etc. have used over 10 000 commercially dyes with production of over 7×10^5 metric tons per year to color final products [1-3]. Reactive dyes are extensively used in textile industries, regarding favorable characteristics such as having bright color, water-soluble and simple application techniques with low energy consumption [2]. About 10–15 % of the dye is lost with a large volume of effluent from textile dyeing processes [1]. It is known that series environmental problems increase with the disposal of such effluents into natural aquatic ecosystems. Apart from the toxicological properties of some dyes, color is one of the first signs of contamination in wastewater. Since a very small quantity of dyes in water can be visible, it often affects the aesthetic merit and water transparency which has adverse influences on photosynthetic activity due to reduction of light penetration [4].

Degradation of reactive dyes is very difficult because they are designed to stabilize and to resist for fading against exposure to sweat, light, water and oxidizing agents [5]. Therefore, the removal of reactive dyes from wastewaters has been a main target in many researches in the last few years, not only due to their toxicity, but also because of its visibility. Hence, their removals from industrial effluents have a great importance for aquatic ecosystems before discharging into receiving waters. Physical, chemical and physico-chemical processes are used for treatment of industrial wastewaters [2]. These methods are very costly and create disposal problems due to accumulation of concentrated sludge. Besides, the use of excessive chemical reagents provides a secondary pollution problem and requires additional cost for regeneration of treatment system [6, 7]. Therefore, the search for efficient, eco-friendly and cost-effective remedies for wastewater treatment has been initiated. In the last few years, studies have focused on adsorption of pollutants present in wastewater on biomaterials.

The use of inactive microbial mass and organic materials as biosorbent has many advantages for wastewater treatment: (i) they do not require a continuous supply of nutrients, (ii) they are not affected by toxic wastes, and (iii) these

materials have been shown to accumulate more pollutants than that of organism. Therefore, researchers have focused on biological methods for the treatment of effluents. Biological processes such as bioaccumulation and biodegradation have been proposed as to be a potential process for removing of dyes from bearing wastewaters [4]. The use of biomaterials as adsorbents for the treatment of wastewaters is provided as an alternative method to the conventional treatment. They have many advantages over conventional treatments such as, economical, nontoxic to environment, and widespread [3,8].

Interactions between dyes and biosorbent depend on the nature of dye, specific surface properties of biomass and operating conditions (e.g., pH, temperature, ionic strength). The binding mechanisms of dye to biosorbent vary from physical to chemical [5,6]. The cell wall of algal species has various functional chemical groups such as carboxyl, hydroxyl, amino, thiol, sulphate and phosphate, which are responsible for the sequestration of dye, metal and salt from wastewaters [2,6]. Adsorption of dye on algae depends on the cell wall properties which change from one species to another. Distribution of these functional groups on the surface of cell and their activities may be different for each dye.

Many types of microorganisms have high capacity of dye uptake, such as algae [9], bacteria [10], and fungi [11]. Among these, microalgal biomasses are largely employed as biosorbent for several reasons: such as available in large quantities in nature; largely cultivated worldwide and its processing is relatively cheap. Therefore, microalgal biomass has been successfully used as adsorbent for removing of wastewaters. The binding of dye on inactivated algal biomass depends on the number and type of functional groups on the surface of species and the chemical composition of dye. Even though thousands of algal species are known, only a few of them have been investigated for wastewater treatment [12,13].

Different algal species have been proved to be effective biosorbent for the treatment of wastewaters such as dyes and heavy metals [9,14]. However, there are no detailed studies related with binary adsorption of reactive dyes on *Spirogyra majuscula*. A widespread freshwater alga *S. majuscula* was selected as an effective, natural and cheap adsorbent for removing reactive red (RR) 120 and reactive yellow (RY) 81 dyes, commonly used in textile industry as function of initial dye concentration and pH regimes.

II. MATERIALS AND METHODS

A. Adsorbent

The alga used in this study, *Spirogyra majuscula* [15], was obtained from a freshwater pool in University of Gaziantep (Turkey). The species was filamentous green alga and appeared as an elongated filament composed of cylindrical cells. The alga had spiral chloroplast, end cell wall plane, conjugation tubes occurred from both gametangia and lens-shaped smooth zygospore [16].

Collected *S. majuscula* was washed twice with tap water in order to remove adhering larvae of organisms, soil, etc. After that, it was dried in an oven at 80°C for 24 hours. Powder of this alga was obtained after grinding and sieving (100–75 µm mesh sizes). For the adsorption studies, the adsorbent suspension was prepared as 10 g/L by using the algal powder.

The infrared spectra of the adsorbent were analyzed using a Fourier transform infrared (FTIR) spectrum (Perkin–Elmer Spectrum 100 FTIR Spectrometer) to identify the functional groups responsible for the adsorption.

B. Batch Experiments

Stock dye solution of RR 120 (Procion Red HE-3B; $C_{44}H_{24}Cl_2N_{14}O_{20}S_6Na_6$; Sigma–Aldrich Chemical Co., St. Louis, USA) was prepared in distilled water as 1 g/L. In a similar way, stock solution of RY 81 (Procion Yellow H-E3G, Sigma–Aldrich Chemical Co., St. Louis, USA) was prepared as 1 g/L in distilled water. Each test solution had equal concentration of RR 120 and RY 81. For example, the first test solution included 50 mg/L RR 120 and 50 mg/L RY 81. Other test solutions were prepared in a similar way.

Adsorption studies were performed in 250 mL Erlenmeyer flask containing 100 mL of adsorption solution. Adsorption solution included ten milliliters adsorbent suspension having desired pH (2, 3, 4, and 5) and 90 mL of dyes solution at known initial dye concentration having desired pH (2, 3, 4, and 5) in an Erlenmeyer flask. All the final solutions contained 1.0 g/L adsorbent. The pH of each solution was adjusted to required value with diluted or concentrated HCl and/or NaOH solutions before mixing the adsorbate or adsorbent suspension. The mixtures were agitated on the orbital shaker at 150 rpm for 48 hours to ensure equilibrium was reached.

Samples (5 mL) were taken before mixing of adsorbent suspension with dye bearing solution, then at different time intervals (0.083, 0.17, 0.25, 0.5, 1.0, 2.0, 3.0, 24.0, and 48.0 h) for the determination of residual dye value in the solution. After that, samples were centrifuged to precipitate suspended biomass at 5000 rpm for 5 min. The concentrations of reactive dyes in the supernatant were determined by spectrophotometer (Jenway 6305). Maximum absorbance was observed at 350 and 515 nm for RY 81 and RR 120, respectively. All kinetic experiments were carried out duplicates. The data were the mean values of two replicate determinations.

Amounts of RR 120 or RY 81 uptake per unit of the adsorbent at time t (q_t , mg/g) and at the equilibrium (q_{eq} , mg/g) were calculated by using Eq. (1) and Eq. (2), respectively.

$$q_t = \frac{(C_o - C_t) \times V}{M} \quad (1)$$

$$q_{eq} = \frac{(C_o - C_{eq}) \times V}{M} \quad (2)$$

where C_o , C_t and C_{eq} represent at initial, t time and equilibrium concentrations of RR 120 or RY 81 (mg/L) in

the solution, respectively. V is the volume of solution (L), and M is the mass of adsorbent (g).

C. Statistical Analyses

Analysis of Variance (ANOVA) was performed to determine significant differences for amount of removal dyes as function of initial pH regimes and initial dye concentrations by using the SPSS version 16.0 (SPSS Inc., Chicago, IL, USA). The fitting procedure was performed by using commercial computer software SigmaPlot version 11 (Systat Software, Inc., California, USA) via the Marquardt–Levenberg algorithm.

III. RESULTS AND DISCUSSION

Removals of RR 120 and RY 81 from aqueous solution on dried *S. majuscula* were carried out as a function of initial four dye concentrations, pH regimes and contact time.

FTIR spectrum of the adsorbent with its most abundant functional groups responsible for the adsorption is given in Figure 1. The peak at 3278 cm^{-1} could be attributed to $-\text{OH}$ (hydroxyl) and $-\text{NH}_2$ (amino) groups [15, 17, 18]. The peaks at 2929 cm^{-1} and 1648 cm^{-1} may be attributed to $-\text{C}-\text{H}$ alkane stretches and $-\text{C}=\text{O}$ stretches aldehydes, ketones, carboxylic acid, respectively [17]. The band at 1408 cm^{-1} could be assigned as amid or sulfamide groups [17]. The adsorption peaks at 1033 and 872 cm^{-1} could be attributed to $-\text{C}-\text{O}$ stretches and aromatic $-\text{CH}$ stretching vibrations, respectively [17]. FTIR spectrum of the adsorbent indicated that RR 120 molecules were bounded with the presence of amine and amide groups, which were responsible functional groups, in agreement with findings of Çelekli et al. [19].

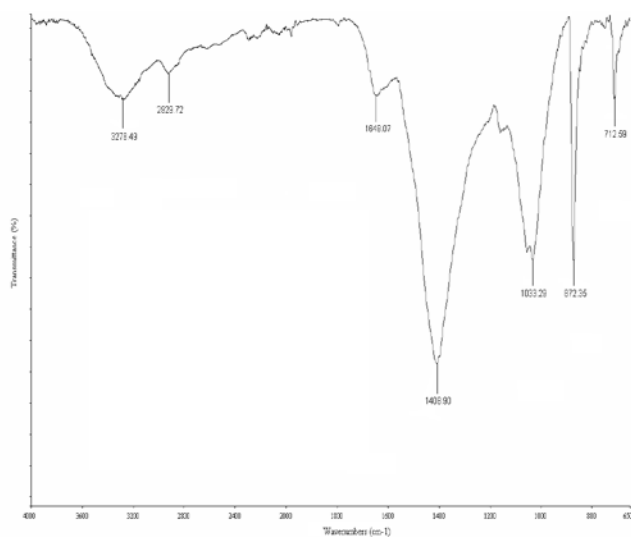


Figure 1 FTIR spectra of *Spirogyra majuscula*

A. Effect of Initial pH Regimes

Change in pH regimes closely affects several functional groups such as amino, carboxyl etc. on the surface of algal cell walls, which are responsible for binding of dye molecules [11, 13].

Effect of pH regimes on the adsorption of reactive dyes on *S. majuscula* is given in Figure 2. Change in pH values

strongly affected ($p < 0.01$) the equilibrium adsorption of both reactive dyes. Increasing initial pH value decreased the amount of adsorbed dyes on the adsorbent. Higher adsorption for these dyes was observed at pH values from 2 to 5 than that of other pH regimes (Figure 2). Therefore, pH values between 2 and 5 were selected for further experiments.

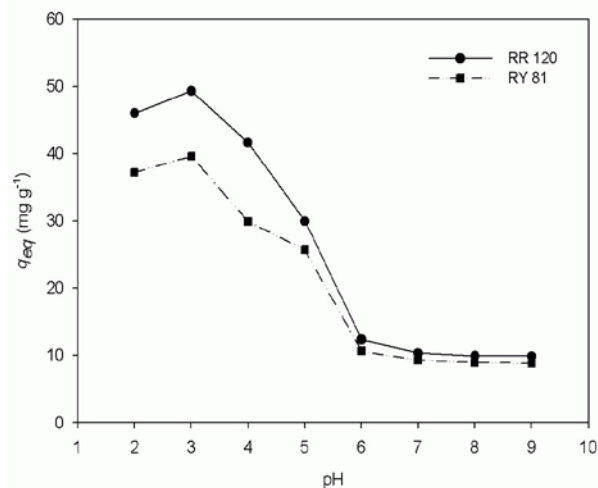


Figure 2 Effect of pH regimes on the adsorption of reactive dyes on *Spirogyra majuscula* ($C_0 = 50\text{ mg/L}$ RR 120 and 50 mg/L RY 81)

Influence of initial pH regimes (pH 2-5) on the adsorptions of RR 120 and RY 81 dyes can be seen in Figures 3 and 4. Equilibrium RR 120 uptake on the green alga was found as 186.95 ± 1.07 , 216.16 ± 0.86 , 152.68 ± 0.99 and $119.88 \pm 0.60\text{ mg/g}$ at pH 2, 3, 4 and 5, respectively. Similarly, adsorption of RY 81 was measured as 163.18 ± 1.46 , 191.75 ± 1.29 , 138.04 ± 2.12 , and $113.46 \pm 1.63\text{ mg/g}$ at pH 2, 3, 4 and 5, respectively. Remarkable adsorption of both reactive dyes was found at initial pH value of 3.0. Likely, Arica and Bayramoğlu [20] reported that maximum adsorption of reactive red 120 on Lentinus sajor-caju was found at pH value of 3.

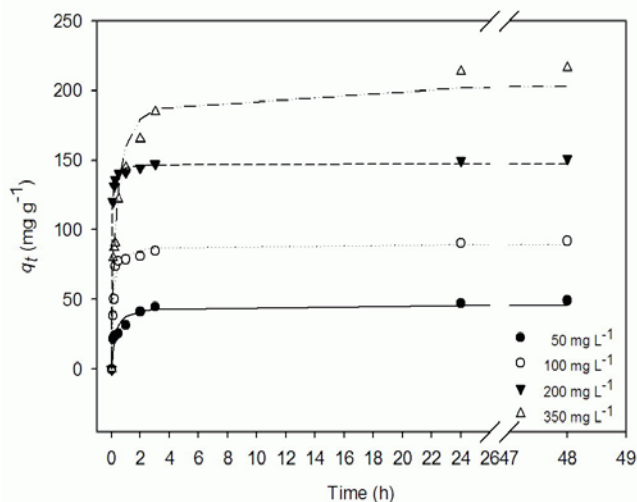


Figure 3 Comparison of experimental points and fitted curves by pseudo second kinetic model for adsorption of RR 120 on *Spirogyra majuscula* at pH 3. Lines show pseudo second kinetic model

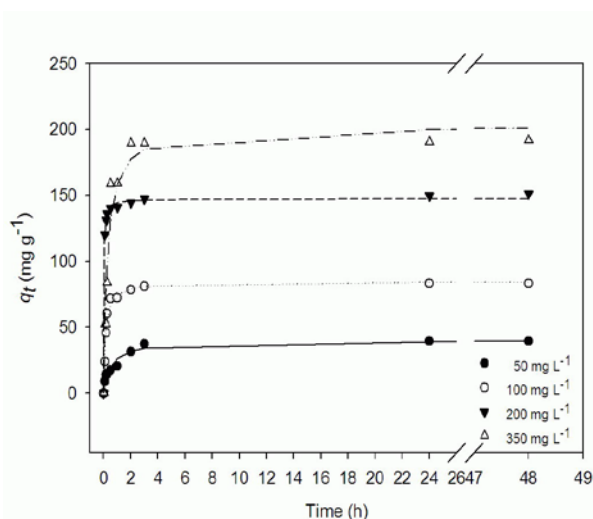


Figure 4 Comparison of experimental points and fitted curves by pseudo second kinetic model for adsorption of RY 81 on *Spirogyra majuscula* at pH 3. Lines show pseudo second kinetic model

Influence of pH on the dye uptake could be explained on the basis of zero point charge (pH_{zpc}) of adsorbent [8, 21]. Çelekli et al. [15] reported that pH_{zpc} of *S. majuscula* was determined as pH 7.7. Surface of adsorbent gets positively charged at pH < pH_{zpc}, which increases the adsorption of dye due to electrostatic forces of attraction. At pH > pH_{zpc}, its surface becomes negatively charged, which adsorbs less dye due to electronic repulsion. Presence of high concentrations of protons at lower pH could neutralize the negatively charged groups and increase number of positively charged groups on the surface of *S. majuscula*, leading to increase adsorption capacity. It was reported that electrostatic attraction could be essential mechanism in the adsorption of pollutants on the alga [8, 13]. However, Aksu and Tezer [5] keynoted that it could be very difficult to explain adsorption mechanism with respect to pH. Since, there are many numbers of variables involved which affect the adsorption of dye such as the number and type of

functional groups on the adsorbent surface, water chemistry, ionic strength etc. [22].

B. Effects of Contact Time and Initial Dye Concentration

Binary adsorption of RR 120 and RY 81 dyes at different initial dye concentrations were performed on *S. majuscula* during 48 h of contact time. Adsorption of these dyes increased ($p < 0.01$) with increasing contact time. Rapid adsorption was observed during the first 30 min. After then, removal rate of dyes reduced gradually until the equilibrium state. There was no significant difference ($p > 0.05$) in the amount of removing dyes in this state.

Adsorption capacity of the adsorbent was increased with increasing concentrations of dyes (Figures 3 and 4), as a result of increase in the driving forces [11, 23]. *S. majuscula* had remarkable potential for the removal of reactive dyes from aqueous adsorption solution in the binary system when compared with previous studies in single adsorption system [20, 22]. Although there could be a competitive adsorption of reactive dyes on the surface of the alga, the adsorption capacity of *S. majuscula* for RR 120 in binary adsorption system was found to be higher than that of adsorption on *L. sajor-caju* in single dye adsorption system [20]. This could be due to having differences in the surface properties of each adsorbent such as functional groups, surface area, particle size, concentration etc. and other environmental conditions.

C. Kinetic Modeling

Adsorption kinetics of RR 120 and RY 81 dyes has been carried out to understand the adsorption behavior of dried *S. majuscula* with respect to contact time, initial dye concentrations and pH regimes. In the present study, pseudo first-order [24] and second-order kinetic [25] models (Table 1) were used to describe the behavior of batch adsorption experiments.

Table I EQUATIONS OF MODELS AND ERROR FUNCTION

Kinetic Models	References	Equation and Number
Pseudo first-order kinetics	[24]	$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2.303} t$ (3)
Pseudo second-order kinetics	[25]	$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}$ (4)
Equilibrium Models	References	Equation and number
Langmuir	[26]	$q_{eq} = \frac{b q_o C_{eq}}{1 + b C_{eq}}$ (5)
Freundlich	[27]	$q_{eq} = K_F C_{eq}^{1/n}$ (6)
Redlich-Peterson	[28]	$q_{eq} = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^\beta}$ (7)
Error function	Reference	Equation and number

Chi-square statistic

[8]

$$\chi^2 = \sum_{i=1}^m [(q_{\text{exp}} - q_{\text{cal}})^2 / q_{\text{cal}}] \quad (8)$$

Symbols' of parameters are given in Abbreviation section.

Values of pseudo first and second-order kinetic model are presented in Table 2. Pseudo first-order kinetic model could only describe the adsorption of RR 120 and RY 81 up to 30 min, respectively, where rapid adsorption occurred

[25]. It could be concluded that this model was not suitable to describe adsorption of both reactive dyes on *S. majuscula* for the whole adsorption process. Similar results were also observed in the Literatures [8, 23].

Table II KINETIC PARAMETERS FOR THE ADSORPTION OF RR 120 AND RY 81 ON *SPIROGYRA MAJUSCULA*

Reactive Red 120									Reactive Yellow 81						
		Pseudo First Kinetic				Pseudo Second Kinetic			Pseudo First Kinetic				Pseudo Second kinetic		
C_o	pH	q_{exp}	k_1	q_{cal}	R^2	k_2	q_{cal}	R^2	q_{exp}	k_1	q_{cal}	R^2	k_2	q_{cal}	R^2
50	2	45.96	0.2193	41.377	0.940	0.0089	43.307	0.980	37.18	0.1139	33.488	0.900	0.0047	35.628	0.964
	3	49.34	0.0532	42.875	0.815	0.0017	45.949	0.912	39.61	0.0201	37.875	0.914	0.0008	39.978	0.953
	4	41.64	0.0569	37.916	0.950	0.0021	40.381	0.986	29.89	0.0359	29.660	0.983	0.0016	31.634	0.972
	5	29.95	0.0368	24.940	0.782	0.0018	27.286	0.895	25.69	0.0199	24.306	0.817	0.0014	25.221	0.868
100	2	81.37	0.1110	65.110	0.754	0.0020	70.557	0.864	74.41	0.0763	58.510	0.858	0.0016	63.427	0.934
	3	92.02	0.1071	85.051	0.967	0.0019	89.655	0.976	83.25	0.0831	79.776	0.986	0.0014	84.661	0.982
	4	72.72	0.0225	64.720	0.779	0.0006	68.260	0.878	65.66	0.0366	64.223	0.979	0.0008	68.673	0.985
	5	56.47	0.0255	50.272	0.945	0.0006	55.267	0.983	55.77	0.1405	53.329	0.982	0.0043	55.808	0.993
200	2	138.08	0.1136	121.388	0.856	0.0013	129.104	0.940	74.41	0.0763	58.510	0.858	0.0016	63.427	0.934
	3	151.16	0.3362	143.674	0.987	0.0056	147.513	0.998	83.25	0.0831	79.776	0.986	0.0014	84.661	0.982
	4	111.36	0.1444	101.510	0.943	0.0022	106.964	0.985	65.66	0.0366	64.223	0.979	0.0008	68.673	0.985
	5	92.17	0.0257	83.473	0.931	0.0004	90.405	0.981	55.77	0.1405	53.329	0.982	0.0043	55.808	0.993
350	2	186.95	0.0592	175.502	0.944	0.0005	186.486	0.971	163.18	0.0551	157.200	0.934	0.0005	166.718	0.957
	3	216.16	0.0447	188.318	0.874	0.0003	204.040	0.951	191.75	0.0438	188.873	0.974	0.0003	202.112	0.959
	4	152.68	0.0492	137.401	0.892	0.0005	147.478	0.960	138.04	0.0323	132.015	0.974	0.0003	142.940	0.977
	5	119.88	0.2154	104.754	0.904	0.0033	110.137	0.956	113.46	0.0845	103.381	0.923	0.0011	110.058	0.961

Symbols' of parameters are given in Abbreviation section.

Pseudo second-order model is related to the adsorption capacity of adsorbent [25]. The straight-line of t/q_t against t plots (not shown) indicated the ability of this model to describe the experimental kinetic data. Besides, correlation between the experimental and predicted q_t data from pseudo second kinetic model can be seen in Figures 3 and 4. It can be concluded that pseudo second-order kinetic model could be regarded as sufficient to describe the adsorption of these dyes on *S. majuscula*. In the literature, this model has adequately described adsorption of dyes [8, 15].

D. Equilibrium Modeling

Langmuir [26], Freundlich [27], and Redlich–Peterson [28] (Table 1) were fitted to describe equilibrium adsorption between adsorbed material on biomass (q_{eq} , mg/g) and unadsorbed pollutant in solution (C_{eq} , mg/L). Langmuir model can be expressed by means of a dimensionless

constant, RL [19, 29], whose magnitude provides information about whether the adsorption process is spontaneous or non-spontaneous.

Results of Langmuir, Freundlich, and Redlich–Peterson models are summarized in Table 3. Langmuir parameters, q_o and b , were found to be higher at pH 3 than those of other pH regimes for both reactive dyes. Maximum adsorption capacity of *S. majuscula* was calculated from Langmuir model as 273.30 mg g⁻¹ and 301.16 mg g⁻¹ for RR 120 and RY 81, respectively (Table 3). Difference in dye uptake capacity of *S. majuscula* could be consequence of the properties of reactive dyes such as the structural, chemical composition etc. Despite, there was a competition of reactive dyes to bind the surface of the alga in binary system, *S. majuscula* showed remarkable adsorption capacity compared to the single anionic dye adsorption system in the Literatures [8, 11, 20, 30]. Values of RL were

found to be between 0.10 and 0.70 for RR 120 and 0.24 and 0.78 for RY 81, respectively. Due to its values between 0

and 1, these adsorption processes are favorable, in agreement with findings of previous studies [8, 20, 29].

Table III RESULTS OF ISOTHERMS FOR THE REMOVAL OF RR 120 AND RY81 ON *SPIROGYRA MAJUSCULA*

Reactive Red 120					
Isotherm	pH	2	3	4	5
Langmuir	q_o	251.94	273.30	189.55	182.94
	b	0.0169	0.0248	0.0169	0.0008
	R_L	0.24–0.54	0.10–0.45	0.15–0.54	0.25–0.70
	R^2	0.976	0.969	0.977	0.998
	χ^2	7.5814	14.6366	2.9812	0.1767
Freundlich	K_F	16.8	24.908	14.118	6.312
	n	2.102	2.277	2.24	1.831
	R^2	0.989	0.995	0.999	0.974
	χ^2	1.1418	0.6781	0.1160	2.1034
Redlich-Peterson	K_{R-P}	112.309	140.847	14.564	69.013
	a_{R-P}	6.271	5.223	0.706	10.521
	β	0.05349	0.05749	0.0616	0.04595
	R^2	0.989	0.995	0.999	0.974
	χ^2	1.1244	0.6631	0.0045	2.0719
Reactive Yellow 81					
Isotherm	pH	2	3	4	5
Langmuir	q_o	254.77	301.16	225.09	192.77
	b	0.0089	0.0092	0.0071	0.0057
	R_L	0.24–0.69	0.24–0.68	0.29–0.74	0.33–0.78
	R^2	0.989	0.985	0.957	0.953
	χ^2	1.1430	6.4914	6.1802	7.7502
Freundlich model	K_F	8.675	11.025	6.309	4.432
	n	1.801	1.769	1.754	1.702
	R^2	0.956	0.947	0.909	0.908
	χ^2	4.9470	14.5843	11.5335	12.5023
Redlich-Peterson	K_{R-P}	43.779	90.632	63.878	58.871
	a_{R-P}	4.613	8.571	9.693	12.788
	β	0.0546	0.0443	0.0436	0.0417
	R^2	0.957	0.948	0.909	0.908
	χ^2	4.8179	14.4260	11.4609	12.4644

Symbols' of parameters are given in Abbreviation section.

The highest values of KF from Freundlich model were found at initial pH 3 for reactive dyes. Magnitudes of KF and n, which showed easy separation of RR 120 and RY 81 dyes from aqueous solution, indicated high adsorption capacity of *S. majuscula*. Similar results were also found in the Literatures [3, 8, 24].

Values of KR-P obtained from Redlich-Peterson model indicated that adsorption of *S. majuscula* was found to be higher for RR 120 than that for RY 81 except at pH 4 (Table 3). Values of β lied between 0 and 1, which indicated adsorptions are favorable.

Plots of q_{eq} against C_{eq} (Figures 5 and 6) indicated applicability of Langmuir, Freundlich, and Redlich-Peterson models. Experimental data were fitted to the aforementioned models which had high correlation coefficients (Table 3, Figures 5 and 6). Applicability of these models was also observed in previous adsorption studies [7, 8, 11]. Results of correlation coefficient and the error functions (Table 3) showed that Freundlich and Redlich-Peterson models were more appropriate to describe the adsorption of RR 120. On the other hand, Langmuir model was the most appropriate model to describe the adsorption of RY 81, which implied a homogeneous sorption phenomenon such as equally

available adsorption sites, monolayer surface coverage and no interaction between adsorbed species.

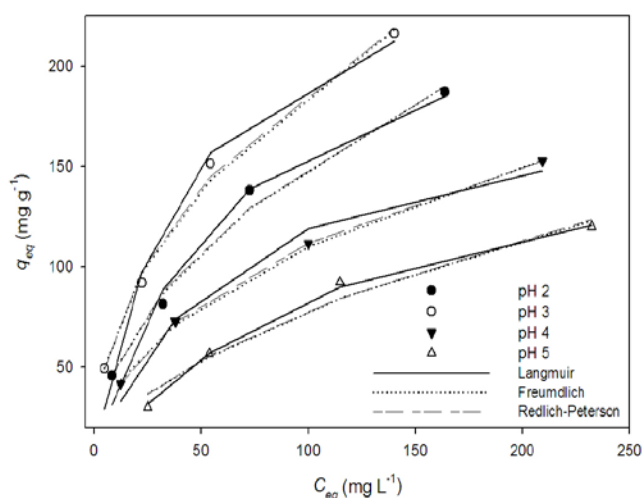


Figure 5 Comparison of experimental symbols and fitted lines by Langmuir, Freundlich and Redlich–Peterson models for adsorption of RR 120

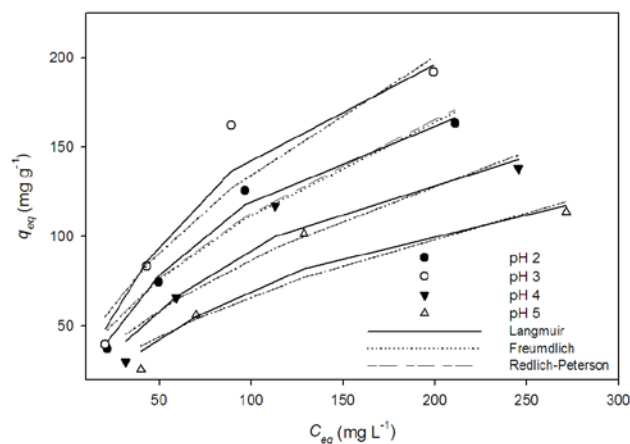


Figure 6 Comparison of experimental symbols and fitted lines by Langmuir, Freundlich and Redlich-Peterson models for adsorption of RY81

IV. CONCLUSIONS

The present study showed that *S. majuscula* had a huge potential for binary uptake of RR 120 and RY 81 dyes from aqueous solution. Behavior of batch sorption kinetics was well described by pseudo second-order kinetic model. Higher R^2 values and lower values of error functions indicated that Freundlich and Redlich-Peterson models were more suitable for adsorption of RR 120, while Langmuir model was more appropriate for adsorption of RY 81. This species could have high potential for treatment of textiles wastewater in industrial scale as effective and natural adsorbent without excessive cost.

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REFERENCES

- [1] Zollinger, H. (1987). Azo dyes and pigments. Colour chemistry-synthesis, properties and applications of organic dyes and pigments. New York: VCH.
- [2] Aksu, Z. (2005). Application of biosorption for the removal of organic pollutants: a review. *Process Biochemistry*, 40: 997–1026.
- [3] Vijayaraghavan, K. and Y.S. Yun (2008). Biosorption of C.I. Reactive Black 5 from aqueous solution using acid-treated biomass of brown seaweed *Laminaria sp.* *Dyes and Pigments*, 76: 726–732.
- [4] Robinson, T., G. McMullan, R. Marchant and P. Nigam (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, 77, 247–255.
- [5] Aksu, Z. and S. Tezer (2005). Biosorption of reactive dyes on the green alga *Chlorella vulgaris*. *Process Biochemistry*, 40: 1347–1361.
- [6] Crini, G. (2006) Non-conventional low-cost adsorbents for dye removal: a review. *Bioresource Technology*, 97: 1061–1085.
- [7] Lakshmi, U.R., V.C. Srivastava, I.D. Mall and D.H. Lataye (2009). Rice husk ash as an effective adsorbent: Evaluation of adsorptive characteristics for Indigo Carmine dye. *Journal of Environmental Management*, 90: 710–720.
- [8] Li, Y., J., Zhang C., Zhang L., Wang and B. Zhang (2008). Biosorption of methylene blue from aqueous solution by softstem bulrush (*Scirpus tabernaemontani* Gmel.). *Journal of Chemical Technology and Biotechnology*, 83: 1639–1647.
- [9] Kumar, K.V., V. Ramamurthi and S. Sivanesan (2006). Biosorption of malachite green, a cationic dye onto *Pithophora sp.*, a freshwater alga. *Dyes and Pigments*, 69: 102–107.
- [10] Chen, K.C., J.Y. Wu, D.J. Liu and S.C.J. Hwang (2003). Decolorisation of the textile dyes by newly isolated bacterial strains. *Journal of Biotechnology* 101: 57–68.
- [11] Aksu, Z. and G. Karabayir (2008). Comparison of biosorption properties of different kinds of fungi for the removal of gryfalan black RL metal-complex dye. *Bioresource Technology*, 99(16): 7730–7741.
- [12] Marungueng, K. and P. Pavasant (2006). Removal of basic dye (astrazon blue FGRL) using macroalga *Caulerpa lentillifera*. *Journal of Environmental Management*, 78: 268–274.
- [13] Aravindhan, R., J.R. Rao and B.U. Nair (2007). Removal of basic yellow dye from aqueous solution by sorption on green alga *Caulerpa scalpelliformis*. *Journal of Hazardous Materials*, 142: 68–76.
- [14] Dönmez, G. and Z. Aksu (2002). Removal of chromium (VI) from wastewaters by *Dunaliella* species. *Process Biochemistry*, 38: 751–762.
- [15] Çelekli, A., M. Yavuzatmaca and H. Bozkurt (2009). Kinetic and equilibrium studies on biosorption of reactive red 120 from aqueous solution on *Spirogyra majuscula*. *Chemical Engineering Journal*, 152: 139–145.
- [16] Çelekli, A., O. Obalı and O. Külköylüoğlu (2007). The phytoplankton community (except Bacillariophyceae) of Lake Abant (Bolu, Turkey). *Turkish Journal of Botany*, 31: 109–124.
- [17] Arief, V.O., K. Trilestari, J. Sunarso, N. Indraswati and S. Ismadi (2008). Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: characterization, biosorption parameters and mechanism studies: a review. *Clean*, 36: 937–962.
- [18] A. Çelekli, M. Yavuzatmaca and H. Bozkurt (2010). An ecofriendly process: predictive modelling of copper adsorption from aqueous solution on *Spirulina platensis*. *Journal of Hazardous Materials*, 173: 123–129.
- [19] Çelekli, A., B. Tanrıverdi and H. Bozkurt (2011). Predictive modeling of removal of Lanaset Red G on *Chara contraria*; kinetic, equilibrium, and thermodynamic studies. *Chemical Engineering Journal*, 169: 166–172.
- [20] Arica, M.Y. and G. Bayramoğlu (2007). Biosorption of Reactive Red-120 dye from aqueous solution by native and modified fungus biomass preparations of *Lentinus sajor-caju*. *Journal of Hazardous Materials*, 149: 499–507.

- [21] Kumar, K.V. and K. Porkodi (2007). Mass transfer, kinetics and equilibrium studies for the biosorption of methylene blue using *Paspalum notatum*. *Journal of Hazardous Materials*, 146: 214-226.
- [22] Han, R., P. Han, Z. Cai, Z. Zhao and M. Tang (2008). Kinetics and isotherms of neutral red adsorption on peanut husk. *Journal of Environmental Science*, 20: 1035-1041.
- [23] Mane, V.S., I.D. Mall and V.C. Srivastava (2007). Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash. *Journal of Environmental Management*, 84: 390-400.
- [24] Lagergren, S. (1898). Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens. Handlingar*, 24: 1-39.
- [25] Ho, Y.S. and G. McKay (1999). Pseudo second-order model for sorption processes. *Process Biochemistry*, 34: 451-465.
- [26] Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica, and platinum. *Journal of American Chemical Society*, 40: 1361-1368.
- [27] Freundlich, H. (1907). Ueber die adsorption in Lösungen. *Z. Phys. Chem.* 57A: 385-470.
- [28] Redlich, O.J. and D.L. Peterson (1959). A useful adsorption isotherm. *J. Phys. Chem.* 63: 1024.
- [29] Leechart, P., W. Nakbanpote and P. Thiravetyan (2009). Application of waste wood-shaving bottom ash for adsorption of azo reactive dye. *Journal of Environmental Management*, 90: 912-920.
- [30] Çelekli, A., M. Yavuzatmaca and H. Bozkurt (2010). Modelling for removing of reactive red 120 on pistachio husk. *Clean*, 38(2): 173-180.



Abuzer Çelekli, graduated from Department of Biology, University of Ankara. He received his M.Sc. in Microalgal Biotechnology from University of Ankara and his Ph.D. in Ecology, Statistic and taxonomy of phytoplankton from University of Abant İzzet Baysal. At present, he is an Assoc. Prof. Dr. of bioprocess engineering about wastewater treatment and biomass production, ecology and taxonomy of algae in University of Gaziantep. Now, he has published his work in more than 23 international papers, and has presented her work in 6 international conferences and more than 25 national conferences.